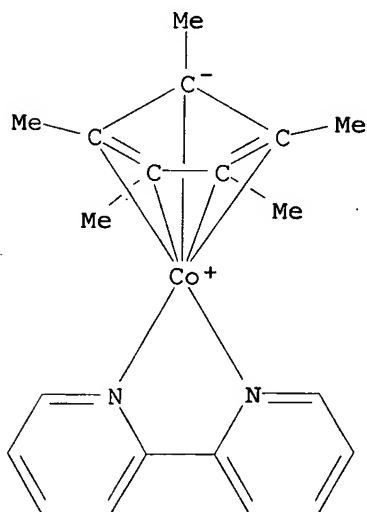


L16 ANSWER 131 OF 260 REGISTRY COPYRIGHT 2007 ACS on STN
 RN 186599-61-1 REGISTRY
 ED Entered STN: 27 Feb 1997
 CN Cobalt, (2,2'-bipyridine-κN1,κN1')[(1,2,3,4,5-η)-1,2,3,4,5-pentamethyl-2,4-cyclopentadien-1-yl]- (9CI) (CA INDEX NAME)
 MF C20 H23 Co N2
 CI CCS
 SR CA
 LC STN Files: CA, CAPLUS
 DT.CA Caplus document type: Journal
 RL.NP Roles from non-patents: FORM (Formation, nonpreparative); PREP (Preparation); PROC (Process); PRP (Properties)

Ring System Data

Elemental Analysis EA	Elemental Sequence ES	Size of the Rings SZ	Ring System Formula RF	Ring Identifier RID	RID Occurrence Count
C2Co-C2Co- C2Co-C2Co- C2Co-C2CoN2- C5N-C5N	CoC2-CoC2- CoC2-CoC2- CoC2-CoNC2N- NC5-NC5	3-3-3-3-3-5- 6-6	C15CoN2	4607.1.1	1



3 REFERENCES IN FILE CA (1907 TO DATE)
 3 REFERENCES IN FILE CAPLUS (1907 TO DATE)

REFERENCE 1

AN 142:114242 CA <<LOGINID::20070215>>
 TI Reduced and excited states of the intermediates (α-diimine)(C5R5)Rh in hydride transfer catalysis schemes: EPR and resonance Raman spectroscopy, and comparative DFT calculations of Co, Rh and Ir analogues
 AU Sieger, Monika; Kaim, Wolfgang; Stufkens, Derk J.; Snoeck, Theo L.; Stoll, Hermann; Zalis, Stanislav
 CS Institut fuer Anorganische Chemie, Universitaet Stuttgart, Stuttgart, D-70550, Germany
 SO Dalton Transactions (2004), (22), 3815-3821

CODEN: DTARAF; ISSN: 1477-9226

PB Royal Society of Chemistry

DT Journal

LA English

CC 29-13 (Organometallic and Organometalloidal Compounds)

Section cross-reference(s): 22, 77

AB The electronic structures of the highly air-sensitive intermediates (N-N)(C5Me5)Rh, (N-N = 2,2'-bipyridine (bpy), 2,2'-bipyrimidine (bpym), 2,2'-bipyrazine (bpz) and 3,3'-bipyridazine (bpdz)) of hydride transfer catalysis schemes were studied through resonance Raman (rR) spectroscopy and through EPR of the reduced forms [(N-N)(C5Me5)Rh]^{o-}. The rR results are compatible with a predominant MLCT character of the lowest excited states [(N-N)(C5Me5)Rh]^{*}, and the EPR spectra of the reduced states reveal the presence of anion radical ligands, (N-N)^{o-}, coordinated by unusually electron rich rhodium(I) centers. The exptl. results, including the assignments of electronic transitions, are supported by DFT calcns. for the model compds. [(N-N)(C5H5)Rh]^{o/o-}, N-N = bpy or bpym. The calcns. confirm a significant but not complete mixing of metal and ligand orbitals in the LUMO which still retains about 3/4 $\pi^*(N-N)$ character. DFT calcns. on (bpy)(C5H5)M and [(bpy)(C5H5)ClM]⁺, M = Co, Rh, Ir, agree with the exptl. results such as the differences between the homologues, especially the different LUMO characters

of the precursor cations in the case of Co ($\rightarrow dM$) and Rh or Ir ($\rightarrow \pi^*(bpy)$).

ST reduced excited state intermediate diimine cyclopentadienyl rhodium hydride transfer; catalysis hydride transfer diimine cyclopentadienyl rhodium complex; EPR resonance Raman spectra DFT diimine rhodium cobalt iridium

IT Density functional theory

(B3LYP; reduced and excited states of intermediates in cyclopentadienylrhodium diimine in hydride transfer catalysis schemes and EPR, resonance Raman spectroscopy, and comparative DFT calcns. of cobalt, rhodium and iridium analogs)

IT Charge transfer transition

ESR (electron spin resonance)

Electronic structure

Electronic transition

Excited state

Hydride transfer catalysts

LUMO (molecular orbital)

Resonance Raman spectra

(reduced and excited states of intermediates in cyclopentadienylrhodium diimine in hydride transfer catalysis schemes and EPR, resonance Raman spectroscopy, and comparative DFT calcns. of cobalt, rhodium and iridium analogs)

IT Raman spectroscopy

(resonance; reduced and excited states of intermediates in cyclopentadienylrhodium diimine in hydride transfer catalysis schemes and EPR, resonance Raman spectroscopy, and comparative DFT calcns. of cobalt, rhodium and iridium analogs)

IT 108120-99-6 108121-03-5 138749-28-7 138749-30-1

RL: CPS (Chemical process); PEP (Physical, engineering or chemical process); PRP (Properties); RCT (Reactant); PROC (Process); RACT (Reactant or reagent)

(reduced and excited states of intermediates in cyclopentadienylrhodium diimine in hydride transfer catalysis schemes and EPR, resonance Raman spectroscopy, and comparative DFT calcns. of cobalt, rhodium and iridium analogs)

IT 34475-06-4 46930-73-8 64506-26-9 84180-60-9 91742-27-7

93560-38-4 95392-53-3 102211-72-3 108120-95-2 123421-11-4

145638-41-1 178316-74-0 186599-61-1 603136-08-9 603136-09-0

820969-51-5 820969-55-9 820969-68-4 820969-69-5 820969-70-8

820969-71-9 820969-72-0 820969-73-1

RL: FMU (Formation, unclassified); PRP (Properties); FORM (Formation, nonpreparative)

(reduced and excited states of intermediates in cyclopentadienylrhodium diimine in hydride transfer catalysis schemes and EPR, resonance Raman spectroscopy, and comparative DFT calcns. of cobalt, rhodium and iridium analogs)

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REFERENCE 2

AN 132:293866 CA <<LOGINID::20070215>>
TI Synthesis, Structure, and Reactivity of [C5Me5CoLL'] Complexes with L =
Pyridine and L' = Olefin or L-L' = Bipyridine
AU Lenges, Christian P.; White, Peter S.; Marshall, Will J.; Brookhart,
Maurice
CS Department of Chemistry Venable and Kenan Laboratories, The University of
North Carolina at Chapel Hill, Chapel Hill, NC, 27599-3290, USA
SO Organometallics (2000), 19(7), 1247-1254
CODEN: ORGND7; ISSN: 0276-7333
PB American Chemical Society
DT Journal

LA English

CC 29-13 (Organometallic and Organometalloidal Compounds)
Section cross-reference(s): 75

AB The bis(olefin) complex $[C_5Me_5Co(C_2H_3SiMe_3)_2]$ (6) reacts with pyridine at 22° to give the pyridine olefin complex $[C_5Me_5Co(C_2H_3SiMe_3)(C_5H_5N)]$ (7). The addition of excess pyridine does not result in the formation of a bis(pyridine) adduct. Thermolysis of solns. of 7 in benzene-d₆ results in catalytic H/D exchange which incorporates deuterium from the solvent into coordinated olefin. Pyridine dissociation generates a 16-electron intermediate which is formulated as the reactive species. At long times deuteration of the coordinated pyridine is also observed via shuttling of deuterium from the solvent to the olefin ligand and then to the pyridine. The reaction of 6 with pyridine-d₅ results in the analog 7-d₅. Thermolysis of 7-d₅ shows preference for H/D exchange at the ortho positions of coordinated pyridine, which has been explained by the formation of η^2 -coordinated intermediates. Reaction of 4-phenylpyridine with 6 yields the analogous pyridine adduct $[C_5Me_5Co(C_2H_3SiMe_3)(4-C_6H_5-C_5H_4N)]$ (12), which was characterized by x-ray structural anal. H/D exchange catalysis is also observed using this pyridine derivative. In a reaction of bipyridine with 6 clean olefin substitution is observed at 22° to generate violet, highly air sensitive $[C_5Me_5Co(bipy)]$ (13). Complex 13 has been characterized by x-ray structural anal.

ST silylvinyl cobalt cyclopentadienyl complex reaction pyridine bipyridine; pentamethylcyclopentadienylcobalt silylvinyl pyridine complex prepn hydrogen deuterium exchange; crystal mol structure silylvinyl phenylpyridine pentamethylcyclopentadienylcobalt bipyridine complex

IT Exchange reaction
(of hydrogen with deuterium; of silylvinyl pentamethylcyclopentadienylcobalt pyridine complexes)

IT Crystal structure
Molecular structure
(of silylvinyl pentamethylcyclopentadienylcobalt phenylpyridine and pentamethylcyclopentadienylcobalt bipyridine complexes)

IT 186599-61-1P
RL: PRP (Properties); SPN (Synthetic preparation); PREP (Preparation)
(preparation and crystal structure of)

IT 264259-98-5P
RL: PRP (Properties); RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(preparation, crystal structure, and hydrogen/deuterium exchange reaction of)

IT 264260-00-6P
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(preparation, thermolysis, and hydrogen/deuterium exchange reaction of)

IT 188827-34-1
RL: RCT (Reactant); RACT (Reactant or reagent)
(reaction with pyridine or bipyridine)

IT 110-86-1, Pyridine, reactions 366-18-7, 2,2'-Bipyridine 939-23-1, 4-Phenylpyridine
RL: RCT (Reactant); RACT (Reactant or reagent)
(synthesis, structure, and reactivity of pentamethylcyclopentadienylcobalt complexes with pyridine, olefin, or bipyridine)

RE.CNT 58 THERE ARE 58 CITED REFERENCES AVAILABLE FOR THIS RECORD

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REFERENCE 3

AN 126:144381 CA <<LOGINID::20070215>>
 TI Electron transfer and chloride ligand dissociation in complexes
 [(C5Me5)ClM(bpy)]+ / [(C5Me5)M(bpy)]n (M = Co, Rh, Ir; n = 2+, +, 0, -): A
 combined electrochemical and spectroscopic investigation
 AU Kaim, Wolfgang; Reinhardt, Ralf; Waldhoer, Eberhard; Fiedler, Jan
 CS Institut fuer Anorganische Chemie der Universitaet, Pfaffenwaldring 55,
 Stuttgart, D-70550, Germany
 SO Journal of Organometallic Chemistry (1996), 524(1-2), 195-202
 CODEN: JORCAI; ISSN: 0022-328X
 PB Elsevier
 DT Journal
 LA English

CC 29-13 (Organometallic and Organometalloidal Compounds)
 Section cross-reference(s): 22, 72, 77

AB In contrast to the rapid and chemical reversible two-electron ECE' reductive elimination reaction $[(C_5Me_5)ClM(bpy)]^+ + 2e^- \rightarrow (C_5Me_5)M(bpy) + Cl^-$, M = Rh or Ir, the analogous cobalt system exhibits two sep. one-electron steps (EC + E' process) with a persistent, EPR-spectroscopically characterized cobalt(II) intermediate $[(C_5Me_5)Co(bpy)]^+$. Within the series of coordinatively unsatd. homologous species $(C_5Me_5)M(bpy)$, the cobalt derivative exhibits the smallest and the iridium homolog the largest metal(I)-to-bpy electron transfer in the ground state, as evident from electrochem. potentials and long-wavelength absorption data. A comparison within that homologous series indicates why the rhodium system, with its intermediate position, is most suitable for hydride transfer catalysis.

ST electron transfer chloride ligand dissoch cyclopentadienylcobalt; cobalt rhodium iridium pentamethylcyclopentadienyl bpy chloride; reductive elimination pentamethylcyclopentadienylcobalt rhodium iridium chloride; electrochem potential pentamethylcyclopentadienylcobalt rhodium iridium chloride; ESR pentamethylcyclopentadienylcobalt rhodium iridium chloride bipyridine

IT Cyclic voltammetry
 ESR (electron spin resonance)
 Electric potential
 Electron transfer
 IR spectra
 (electron transfer and chloride ligand dissociation in complexes pentamethylcyclopentadienylcobalt -rhodium, -iridium chloride bpy complexes by a combined electrochem. and spectroscopic investigation)

IT 90541-04-1 108120-99-6 115565-17-8 138749-27-6 145638-41-1 186599-61-1
 RL: FMU (Formation, unclassified); PEP (Physical, engineering or chemical process); PRP (Properties); FORM (Formation, nonpreparative); PROC (Process)
 (electron transfer and chloride ligand dissociation in complexes pentamethylcyclopentadienylcobalt -rhodium, -iridium chloride bpy complexes by a combined electrochem. and spectroscopic investigation)

IT 366-18-7, 2,2'-Bipyridine
 RL: PEP (Physical, engineering or chemical process); PRP (Properties); RCT (Reactant); PROC (Process); RACT (Reactant or reagent)
 (electron transfer and chloride ligand dissociation in complexes pentamethylcyclopentadienylcobalt -rhodium, -iridium chloride bpy complexes by a combined electrochem. and spectroscopic investigation)

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